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Influence of time on emission of counts in a fresh and an electro-conditioned tube under d. c. excitation*

S. G. PIMPALE

Department of Physics, Barsi College, Barsi-413401, Dist. Sholapur, Maharashtra

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Chemisorption of admixture of gases (air) on glass surface as a determinant of the current pulses (counts) passing through an ozonizer excited by a definite high value of direct current impulse potential, viz. 1.5 kV, has been investigated previously cold worked coaxial cylindrical (fresh) and an electro-conditioned discharge tube. In a fresh tube, the conductivity of discharge counts is found to be exceedingly large; it attains saturation within an appreciably long interval of time and remains unaltered within the experimental accuracy. Compared with the data observed in fresh tube, the count rate remains saturated within an appreciably short time-interval. Thus, for aged air, the discharge counts reached to the minimum stationary value within 6 hours, while for fresh air, it reached within 15 hours. The variation of discharge counts in dark with continuous aging referred to as the pulsed emission phenomenon, follows the postulation of an adsorption-type boundary layer on the annular walls and its characteristic work function. On this consideration, the equations yield,

$$(i)\quad I_s = \frac{I_0.\alpha.\ \exp \int \alpha dx}{\alpha - \beta.\ \exp \int \alpha dx}\ ;\quad (ii)\ S = k(t)^l \text{ and } (iii)\ (\delta I_s) = k'(t)^{1/n}$$

with I_0; I_s; α and β; S; δI_s; m; k and k' as the current pulses without field instantaneous discharge counts; first and second Townsend's coefficent and this first coefficient depends upon the position x in the non-uniform field; amount of adsorbed upto time t; decrease of counts up to time t and lastly constants respectively.

1. INTRODUCTION

The effect of sorbed gases on photo- and thermo-electric currents has been well studied. Cantor (1893) and Knoblauch (1899) observed that substances when exposed to ultraviolet light, lost some negative charges, Chrisler (1908) found that this phenamenon, viz., photo-electric effect, could be eliminated completely, in certain cases, by the removal of occluded gases by scrapping it in vacuum. No photo-electric effect in metals was evident (Kustner 1914). Similarly, when all

*The work reported here was carried out in the Chemistry Department, University of Poona.

occluded gases from potassium are removed, the photo-electric effect disappeared entirely (Wiedemann & Hallawachs 1914). Essentially similar results were obtained by number of other workers (Hennings 1914, Stumf 1914). While the data of the above investigators emphasised the favourable influence of adsorbed gases on photo-electric effect, contrary findings indicating their inhibitory action on electron liberation from metal by irradiation, were also recorded. Thus, Stoletow (1889) found that the photo-electric effect from the platinum incrased when the adsorbed gases were removed by heating it to 200°C, at 700°C the effect was twice than that at laboratory temperature (Zeleny 1901). It was shown that the photo-electric sensitiveness after emission of occluded gases was definitely larger than the effect noted before the expulsion of the gas (Pearsol 1916). The above contradictory results received explanation from the findings due to Peach (1914) that the photo-electric effect of the metal was dependent upon the nature of the gas occluded or adsorbed such as hydrogen, carbon monoxide, oxygen, etc. It has been emphasised by Mallawachs (1932) that electronegative gases cause a decrease and electropositive gases, an increase. Further, a distinction was made between the gas adsorbed on the surface, and those absorbed within the body, of the metal. Adsorbed gases retard the escape of electrons, while the absorbed gases aid the liberation of electrons, apparently by causing some internal agitations (Hallawachs 1932). These views are substantiated by the data on thermo-electric effect. This phenomenon was well investigated by Langmuir (1913, 1914). It was noted that thermo-electric effect of tungsten was markedly inhibited by sorption of O_2; and not restored even when the metal was heated to $>2000°C$ to exclude the adsorbed gas, the irreversible diminution of thermo-electric effect of W by O_2 was attributed to the formation of a compound between W and oxygen. Much advancement in the studies of sorption was achieved by the fundamental investigations of Langmuir. According to Langmuir, there exists a fixed number of atomic groups or sites per unit area of the solid surface, on which alone adsorption of a gas atom or a molecule can take place. These adsorbed atoms, depending upon their electron affinity, retard, as mentioned by Hallawchs (1932), the escape of electrons.

While photo-electric and thermo-electric currents and the influence thereon of adsorbed films received much attention, the variation of the discharge current pulses with the surface nature of the electrodes especially with solid dielectric material, was not fully investigated. It has, however, been mentioned (Loeb 1939) that the discharge current and the mechanisms responsible therefore are markedly dependent upon the work function of the cathode (chiefly the gas adsorbed on it). This factor has now been investigated in some details.

2. Theory and Method of Investigation

In general, there are three processes which occur when a gas is brought in contact with a solid, absorption, diffusion and adsorption (McBain 1938, Laidler

1949). The phenomenon of absorption refers to the intake of gas by the entire bulk, while diffusion deals with the passage of gas atoms or moledules through the intermolecular capillaries, of the solid substance (Lennard 1924). In the last process, adsorption, a known quantity of the gas is taken up by the surface and surface alone of the solid. These three phenomena are summarised by a single name sorption (McBain 1938). Among these, adsorption is of marked importance. It is the only process which is found to occur at ordinary temperatures, with substances like Cu, Al, Au, Ag, Pt, glass, etc. which are in common use as electrode materials and has therefore been studied only in this paper.

Adsorption is principally of two types, the instantaneous and slow process. When a gas is allowed to come in contact with a clear solid surface, a known quantity of it, depending upon the temperature and pressure thereof, is taken up instantaneously (Laidler 1949); in this case, the gas exists in the form of multilayers (Brunauer *et al* 1938, Hill 1947, Cossie 1947, Greg & Jacobs 1948) of molecules held by some monspecific forces (Laidler 1949). This process also referred to as Van der Waal's multimolecular or physical adsorption. This is followed by the slow process; the maximum time necessary for the attainment of saturation is of the order of a few hours to years (Swan & Urquhart 1927) The large time recorded was not due to slow diffusion, since the corresponding constants varied characteristically with pressure. It was further emphasised (Bangham 1928) that the long intervals noted at the saturation time in the slow processes were not untenable from the following theoretical considerations. It is summarised generally (Bamgham 1928, Tompkins & Crawford 1948), following Langmuir, that there are a definite number of atomic groups or sites (small elementry areas) per sq. cm. of solid surface on which sorption of a gas particle can take place. It is further assumed that these atomic groups are unable in their normal condition to adsorb and require first to be activated before they actually combine with or adsorb a molecule or an atom, the necessary energy being obtained from the excited molecules or atoms arriving from the gas phase to the solid surface due to the thermal moments. It has been mentioned above that no sooner that gas is introduced into the system containing nude surface, physical adsorption in which the gas exists in the from of multimolecular layers akin to those of liquid phase, takes place instanstaneously. A molecule or a gas atom with enhanced excitation energy should therefore drive into these layers, reach the Langmuir site transfer its energy to this last. The rate (whenever the rate of sorption is mentioned, it refers to the slow process only and not to the other kind of sorption viz., physical or Van der Waal's adsorption) of sorption depends upon the probability of the excited atoms or molecules reaching the solid surface containing free Langmuir species, small elementary areas), sorption attains saturation when these are completely occupied. Because of this, this process is also referred to as chemisorption, activated adsorption or Langmuir adsorption.

As cited above, the rate of activated adsorption depends upon the probability factor regarding the accessibility of the excited gas particles to the solid surface (Ramaiah 1952). Under contraction (discharge), the population of excited atoms or molecules presumably their reaching the surface, are exceedingly marked; on account of this sorption under (Willow & George 1916, Johnson 1923, Taylor 1928 & Ramaiah 1952) contraction is expected to be very rapid as actually observed. From this it follows that whatever processes that occur under ordinary conditions and during contraction, refer to one and the same phenomenon viz., activated adsorption or Langmuir adsorpton.

The influence of chemisorption on the electrical conductivity of a gas was now investigated. For this purpose the discharge tube was heated for removal adsorbed gases and a known quantity of a gas was introduced therein and excited by a definite potential. The variation of its count rate was studied at regular intervals of time during the progress of sorption under discharge.

3. Experimental

Description of the discharge vessels : Siemen's type discharge tube, formed by sealing together two cylindrical all glass tubes coaxially, was used. This was specially employed for the present studies on account of the fact that no metal surface would come in contact with the gas under investigation. It is well known that the data on sorption of a gas from discharge tube is highly complicated by loss or gain at the metal surface. The use of an ozonizer tube is, however, open to the objection of allowing slight liberation of gases or land formation of certain surface compounds due to the electrolytic nature of the conduction of electricity through glass, under conditions at which the experiments reported herein were carried, the above processes were assumed to be minimum.

Heat treatment: By day-to-day operations of the experimental tube, the surface of the glass walls can be tarnished. With this tarnished electrodes, it is not easy to obtain accurate values of counts since the count rate is often intermittent, presumably due to local changes on surface of the glass walls. It is, therefore, necessary to remove the traces of oxide on the electrode-surface necessary to remove the traces of oxide on the electrode-surface to obtain accurate values of counts. The surfaces of the discharge tube were freed from adsorbed gases by the following process. The discharge tube was heated in a heater box fitted with heater coils and then cooled slowly to the room temperature. This heating at 200°C wipes out its previous history. Thus heating seems to help in bringing the condition of the vessels nearer to that of the fresh one and referred to fresh tube. The tube was then subjected to electrical discharge at room temperature for 15 hours at a continuous potential of 1.5 kV; thereafter the tube was kept unexcited for about 24 hours. This treatment has been called electro-conditioning or aging by earlier workers. The electrode condition of the tube

was checked by observing the count rate at a definite value of discriminator bias (50V) and at a fixed d.c. exciting potential.

Working potential. The discharge tube was excited by a continuous potential of 1.5 kV and the current was measured by a scaler or a Cambridge reflection galvanometer actuated by a crystal detector. The details of these were given in a number of earlier communications (Pimpale 1972, 1973, 1974), and are not reiterated here. While using the ozonizer, the following may be taken into consideration. The ozonizer was worked at potentials above the threshold potential V_{ga} the significance of which for the reactions under discharge in general, and for the phenomenon of Joshi-effect in particular, has been emphasised by Joshi (1928, 1939, 1945). He has shown that in general, the rate of a chemical reaction under discharge, is determined by the potential difference $(V-V_{ga})$ where V is the applied potential employed for studying the reaction. It follows from this that the smaller the difference $(V-V_{ga})$, that is, nearer the potential to V_{ga} the less marked is the rate of the reaction. The potential employed for the present sutdies was maintained very high to the threshold potential, such that the above change would be maximum.

Furthermore, this would facilitate the studies of discharge mostly concerned with the surface of the electrodes, since it was shown (Hennings 1914) that at potentials near V_{ga}, the mechanism related with the cathode, e.g., the liberation of electrons therefrom by positive ionic bombardement and photons ($\mu\theta g$) was predominant, while at large $V > V_{ga}$ the other processes unconnected with the surface and concerned with the gas phase (β) played an important role in the maintenance of the discharge (Bhatawdekar *et al* 1953).

Gas investigated : In the present investigation, dry air at a pressure of 1 mm of mercury enclosed in an annular space of the ozonizer was studied. The experimental set up for the investigation of the variation of count rate with time in heat-treated and untreated discharge tube is shown in figure 1.

Two series of experiments were carried out using fresh and electroconditioned ozonizer. The former had been in use for work on time-variations of discharge counts in air over a period of 15 hours, the latter was electroconditioned.

In the first series of experiments, the count rate at a given counting time, viz., 3 min, was measured with an electronic scaler. At a constant applied continuous potential of 1.5. kV, the counts were observed at intervals of 30 min when the ozonizer was in the dark; these data are presented graphically by a solid curve in figure 2. The course of reaction was expected to be either a progressive diminution of counts or its constancy, depending upon whether the temperature of the system was low enough. Actually, it was found that under the continuous discharge (*cf.* a solid curve in figure 2) the conductivity of discharge counts showed an initial marked rise of counts up to a maximum, it then fell to a minimum, once

again to rise and fall thereafter the conductivity reached the minimum stationary value. The conditions for the optimum development of this periodic effect are such that the corresponding progress of the change is rather slow; thus for instance, in one case as many as 3 well-defined recurrences of conductivity-reversals and of the other electrical quantities mentioned already were obtained necessitating an exposure of 900 minutes to the discharge. After this time, there was slowing down of the change, indicative of a near completion of the reaction.

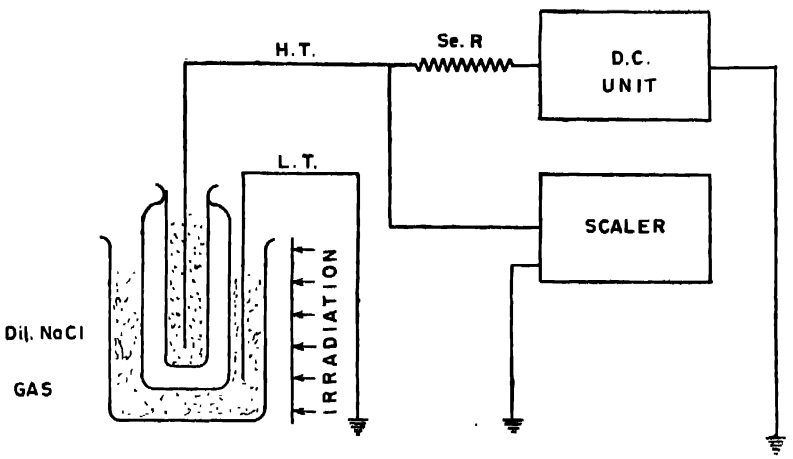

Fig. 1. Studies of pulsed emission decay in an ozonizer discharge.

After one set of experiments, the vessels was unexcited for 24 hours, the discharge was then restarted and the variation of the discharge counts at intervals of 30 min was noted. A dotted curve of figure 2 gives the data obtained with intervals of 30 min. It was interesting to note that the conductivity of the discharge counts was initially exceedingly large at the first instance of recording and decreased rapidly with time. Thus in air, count rate was 164 at $T_m = 0$ min and 1 at 330 min; further exposure to discharge did not alter the conductivity of the discharge counts appreciably.

Compared with the data observed in fresh tube, the count rate attained saturation within and appreciably short time interval. Thus, for aged air, the discharge counts reached the minimum stationary value within 6 hours, while for fresh air, it reached within 15 hours. The minimum stationary value of counts for a fixed electrode separation and gas pressure did not appear to be the same whatever may be the predischarge interval (curves in figure 2). The results in solid curve of figure 2 show that the above time-variation of the discharge counts is markedly affected by heat-treatment. It my be added that the periodic effect, as indicated by the count rate-variation, alternately speeds up and slows down, is not produced when an aged gas is present.

Previously by cold worked ozonizer, the conductivity of the discharge counts was found to be exceedingly large, the conductivity attained saturation within an appreciably long time interval and the conductivity of the discharge counts remained unaltered within the experimental accurancy (*cf.* a solid curve in figure 2)

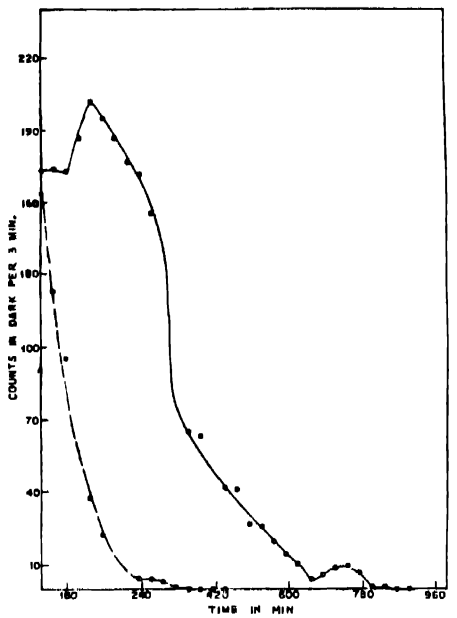

Fig. 2. Current-time characteristics showing pulsed emission decay

3. Discussion

The following are the important conclusions from the foregoing results :

1) The conductivity of the discharge counts I_s of a gas introduced into an intense ionizing zone of a discharge vessel decreases markedly to a minimum value characteristic of the system and pressure.

2) The time-rate of decrease of I_s is exceedingly rapid.

3) The results are markedly affected by heat-treatment. It has been reported in the earlier communications (Loeb 1939, Townsend 1948, Bhatawdekar *et al* 1953), that the (instantaneous) current in a discharge given by

$$I_s = I_0 \frac{(\alpha-\beta).\exp(\alpha-\beta)x}{\alpha-\beta.\exp(\alpha-\beta)x} \qquad (1)$$

Here, $I = n_0.e$ where n_0 is the number of primary electrons, of charge e, to be released from the outer electrode (cathode) surface and responsible for the production of electron avalanches. The Townsend's first coefficient α depends upon the

position x in the nonuniform field. Further, when α is much greater than the second coefficient β, eq. (1) can be written as

$$I_s = I_0 \frac{\alpha.\exp \int \alpha dx}{\alpha - \beta.\exp \int \alpha dx} \qquad (2)$$

From this, it is clear that the count rate and the creation of electron avalanches are fundamentally governed by n_0, α and β. The Townsend's coefficients α and β depend upon the applied field and gas pressure. For a definite potential fed to the discharge tube of known dimensions, the field under the experimental conditions is constant. The gas pressure was observed (Johnson 1923) to decrease with time of exposure to discharge. This aspect was well developed in H_2 by Johnson (1923), the pressure of H_2 as measured by a detector constructed specially for the purpose remained constant when the system was kept unexcited. When the fields were applied, content of the hydrogen decreased rapidly to a minimum value. The reduction was of the order of 0.03-0.04 mm of mercury. The theoretical considerations on contraction in gases suggest that a decrease in gas pressure increases the current as actually observed (Ramaiah 1951). The result (1) reported in this article, the decrease of the conductivity, was attributed to the decrease of primary electrons on account of progressive sorption of gases under contraction (discharge). This is in accord with the observation that photo- and thermo-electric currents decreased with the adsorption of electronegative molecules (or atoms). These last on account of their electron affinit, capture electrons and thus retard their escape from the surface (Hallawach 1932).

The above consideration suggests that if S represents a Langmuir small elementary area (site) on clean glass surface, sorption of air atoms thereon and subsequent capture of electron may be represented as

$$\begin{aligned} S + A^* &\rightarrow S^* + A \\ S^* + A &\rightarrow S \ldots A \\ S \ldots A + e^- &\rightarrow S \ldots A^-. \end{aligned} \qquad \ldots \quad (3)$$

This formation would emphasise that atoms adsorbed on glass retain their electronegative character. This, however, indicates the current view that atoms are held by activated adsortpion on glass by sharing an electron from alkali atom in glass.

The rate of decay in counts gives a striking support for the above view that the adsorbed gas is responsible for the finding (1). It is exceedingly rapid and attained saturation within 900 mins. Essentially similar result viz., rapid rate of sorption under discharge was recorded by a number of investigators. Employing spectroscopic methods Taylor (1928) observed that the disappearance of H_2 in hydrogen

neon tubes was accompanied within 5 mins. As stated above, Johnson (1923) studied the sorption of H_2 under electrodeless discharge and found that the saturation in the pressure-decrease attained within 4 mins.

Further, Bangham (1928) has shown that the rate of sorption of a gas on glass is well represented by the following relationship,

$$S = kt^{\frac{1}{m}}, \qquad \ldots \quad (4)$$

where S is the amount adsorbed upto time t, m and k are constants. This equation was found to be applicable to a number of systems (Bangham & Burt 1924, Francis & Burt 1927) not only with glass as an adsorbent but also with a variety of crystalline and semicrystalline solids.

From the above argument, if we make the assumption that the decrease (δI_s) of the current pulses upto time t is due to the amount of gas adsorbed, one would expect the influence of continuous aging on discharge counts to follow

$$(\delta I_s) = k' t^{\frac{1}{m}}. \qquad \ldots \quad (5)$$

It follows, therefore, that

$$\log (\delta I_s) = \log k' + \frac{1}{m} \log t'. \qquad \ldots \quad (6)$$

It is instructive to note that as required by this relation (6), the plot of log (δI_s) versus log t are sensibly linear for air and also for chlorine and oxygen from published data (Ramanmurty 1948).

It may be mentioned that previously by cold worked tube altered markedly the above data. Similar results were obtained by Ramaiah (1954) in the study of Joshi-effect (Δi). While in electroconditioned ozonizer, the effect could be observed immediately, in heat-treated vessles, a certain amount of aging was found necessary to initiate the rapid decay in counts. The disparity was attributed to the presence of alkali on the surface of former type of ozonizer, which enhanced sorption to aid the occurrence of decay in acounts. Even in the measurements of sorption of gases, the presence of alkali on glass surface played an important role (McBain 1938). Faraday (1830) observed large adsorption of water vapour on glass and attributed it to the existence of alkali. When this was removed by washing glass surface with acids an appreciable sorption was noticed. This catalytic conductivity is however, a general feature of such polar-substances. Knowledge of number of chemical reactions which are controlled by the presence of traces of some polar substance, is available (Dixon 1884, 1898; Miller & Russel 1902). Norrish (1923) has emphasised that the increased activity of gas reactions in the presence of small quantities of NaOH, KCl, etc., is due to distortion on account of the strong local disturbing forces available at the surface of the polar

substance, in the stable configuration of the molecule such that these last become more vulnerable to be attacked. Lennard-Jones & Dent (1924) envisaged the various forces existing outside the surface of the polar substance; (*a*) forces of attraction because of induced dipole in the centre of an atom or ion and the electrostatic field; (*b*) forces due to polarization in the substance by the free charges outside (c) direct electrostatic force between ions in the solid and the free state outside it and (*d*) Van der Waal's forces. Of course, Van der Waal's forces play a primary role, they act as the first agents in the process of adsorption of atom or ion and the electrostatic forces serve to clinch the capture of ultimate adsorption.

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